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**TITLE:** LASER INDUCED PYROLYSIS TECHNIQUES

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## LASER INDUCED PYROLYSIS TECHNIQUES\*

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Since the commercialization of the laser slightly more than 15 years ago, this technology has been applied to many tasks in chemistry. The majority of these utilize the unique monochromaticity of laser radiation. We shall not consider these photochemical studies. Rather we look to the utilization of a laser as a unique tool to rapidly and precisely deposit known amounts of energy into material causing a unique pyrolysis process.

Laser pyrolysis gas chromatography was first reported in the early part of this decade [1-4]. Our initial studies [5], like those of others [6,7], were to characterize polymeric material. Initial results showed that a variety of polymers including those of high thermal stability were readily degraded by a laser beam. Concurrent with these studies were a number of activities designed to determine the nature of laser interactions with matter. For instance, laser induced pyrolysis, conducted within the high vacuum chamber of a mass [8,9] spectrometer, investigated plume velocities. Other workers were tempted to explore the possibilities of chemical synthesis using high power densities emanating from a laser. Several workers point out, for example, that direct transformation of coal into valuable hydrocarbons might be possible [10]. Consequently, papers have appeared concerning laser deposition into coals [11-13]. In addition lasers have also been extensively used for welding and cutting operations. Another area, using extremely high power pulsed laser deposition to initiate nuclear reactions is also being actively explored.

All of these disciplines have contributed to our understanding of the interaction of laser energy with matter [14]. Laser beams are unusual in spectral purity, i.e., narrow band width. Also important, is the fact that the radiation is essentially unidirectional, i.e., a small degree of beam divergence occurs. Thus light propagates in a single direction. This fact suggests that high power densities are possible even for modest devices for the light can be aimed and focused into a sampling location. Equally important is the fact that the energy delivered from pulsed lasers arrives in short times, i.e., narrow pulse length. Thus heating can be done rapidly with very short thermal rise times. Consider now how these properties are utilized in laser pyrolysis.

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## THE LASER PYROLYSIS EVENT

As mentioned previously, considerable work has been reported on laser interactions with matter [15]. It would be incorrect, however, to indicate that these processes, especially with high power devices, are well understood. Clearly the usual models for spectrochemical excitation are only important during initial absorption, for laser deposition typically results in ionization; following that process, absorption by unbound electrons appears to be a primary mechanism.

This can be represented schematically in Figure 1. A normal burst laser, either ruby or Nd-glass (others could be used) is focused and deposited into a sample. The pulse width of such a device is approximately 0.001 sec and frequently energies of about 5 joule/pulse are utilized. Should this energy be focused to a spot diameter of 0.1 cm, the power deposition from that event is  $6.4 \times 10^5$  watt/cm<sup>2</sup>. Q-switched modes lead to powers orders of magnitude greater although total energy may be lower. Power densities of this magnitude result, in part, from the narrow pulse width. This is reflected in a rapid thermal rise time.

Initially a fraction of the energy is absorbed in the sample material. This absorption occurs with high probability at the focal point on the sample. There are several well established mechanisms for this process; probably the best described of these is multi-photon absorption [15]. Data suggest that many classes of compounds which normally show limited

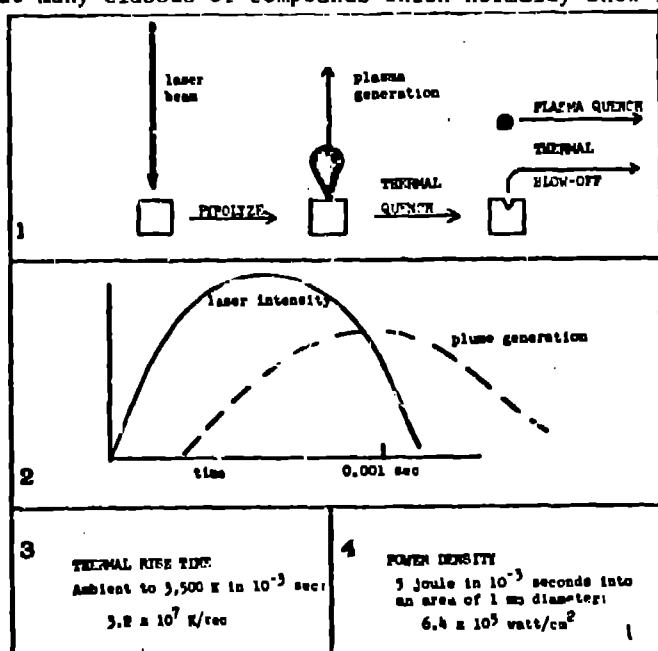


Fig. 1. Representation of Laser Induced Pyrolysis.

Absorption at either 694.3 or 1060 nm, readily absorb ruby and Nd radiation [16]. Through these absorption processes, part of the sample is pumped into a plasma consisting of highly energetic ions, radicals of unusual stability and electrons. This plume grows, during the duration of the event, into the direction of the laser beam. Velocities of plume growth in vacuum are found near  $10^5$  cm/sec [17]. Data show clearly that the absorptivity of light by the plasma is far more probable than in the sample [18]. Thus, during the course of the event, the more energetic fragments move into the beam at the fastest rate absorbing even more energy. The majority of these energetic fragments appear to be electrons; laser energy is converted into electron thermal energy. High pressures resulting from this absorption drive a shock wave into the sample. Electron thermal conductivity is markedly temperature dependent ( $\propto T_e^{5/2}$ ) [18]; rapid heat flow is maintained while the temperature is high and it may be expected that a sharply defined nearly isothermal region results. The temperature of such a high temperature plasma is difficult to estimate; however temperature, as measured by velocities of atomic fragments, is in excess of  $10^5$  K [19]. Modelling this type of process would involve a difficult problem of kinetics and heat transfer. Carbon spectroscopy on the plume shows that molecular fragment concentrations peak following the termination of the pulse. However the entire event is almost as rapid as the pulse width, near 0.001 sec. The thermal fall time is approximately the same as the rise time.

It is of interest to consider how energy leaves the system during the rapid quench following pulse termination. Certainly radiation is one such mechanism. In this case deceleration of electrons is probably an important factor. Collision with cold gas molecules, such as the carrier gas in the inlet port of the GC, is also important. Likewise, wall collisions with the containment quartz tube contribute to energy loss in this rapid quenching process.

#### LASER PYROLYSIS GAS CHROMATOGRAPHY

In laser pyrolysis-gas chromatography one follows the appearance of products after degradation of the sample. Part of the product distribution comes from the quenching of this high temperature plasma. Other products result from thermal shock into the sample. Figure 2 shows results obtained for phenanthrene. The initial intense peak is a mixture of low molecular weight gases- the plasma-quenched products. Following are a series of higher molecular weight compounds. These, typically, are in far lesser amounts than the first group. Shown here are benzene, naphthalene, two different

substituted naphthalenes, the methyl and dimethyl and, in peak 6, the parent species. Fragmentation during this process seems to yield quite simple and predictable patterns. When one ignores the plasma-quenched ensemble, the distributions are not unlike those found in mass spectrometry.

Pyrolysis gas chromatography has clearly shown the effects of heating rates on product distributions. This is especially true when dealing with complex organic molecules for different pyrolytic mechanisms may predominate in different temperature regimes. One is struck by the few products evident [7] in laser-induced pyrolysis compared to the large number found using filament type pyrolyzers. This most probably results from the fact that this "pyrolysis" is most probably primarily a shock phenomenon. These higher molecular weight fragments, the ensemble from the thermal blow off, are a simple and predictable group of products.

There have been several reports on the reproducibility of laser-induced pyrolysis. Data are shown in Table 1. These data [20] were obtained using a thin section of a polymeric material. The laser beam was used to drill a hole through the material. As can be seen, for the four peaks detected, reproducibility approaches the stated accuracy of the integrator used for these studies. This conclusion has not been always reached, however [20]. Reproducibility of this method depends upon a number of factors including the optical system. It depends upon the pulse energy and how that energy

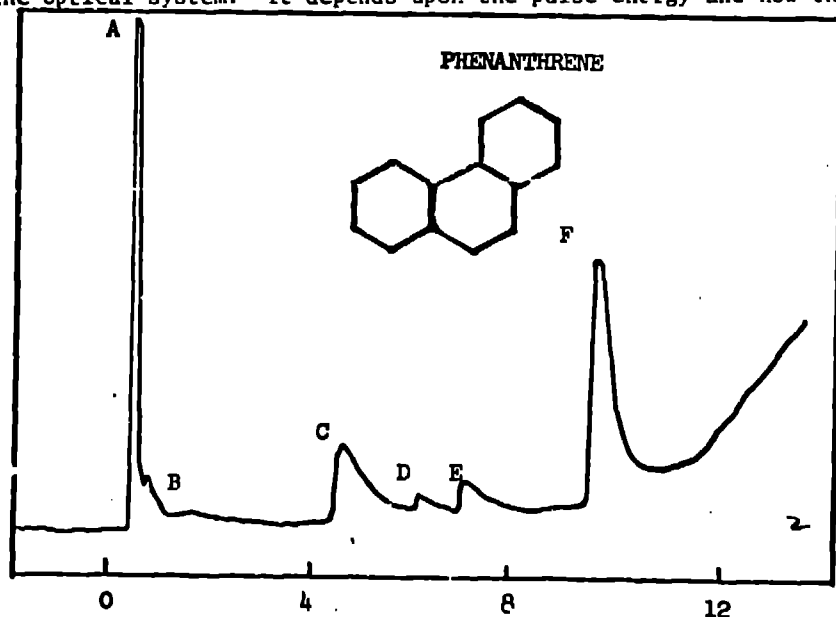


Fig. 2. Laser Pyrogram of Phenanthrene. Products Separated on Apiezon N. Peak Identification: A= methane, ethylene, acetylene (main), butadiene, B= benzene, C= naphthalene, D= methyl naphthalene, E= dimethylnaphthalene, F= phenanthrene (parent).

Table 1

Reproducibility of Laser-Induced Pyrograms: Analysis of Low Molecular Weight Peaks

Peak No.	Area $\Sigma$ (Uncorrected)	$\Sigma$ Rel. Dev.
1	$3.26 \pm 0.17^*$	5.2
2	$60.27 \pm 0.75$	1.2
3	$12.83 \pm 0.58$	4.5
4	$23.61 \pm 0.52$	2.2
Total Area (Counts)	$10,801 \pm 3.200$	29.6

\*1 Standard deviation.

Sample - Polymeric (PVC-PE) Tubing

Radiation: 693 nm (Ruby)

is deposited into the sample. The type of data analysis, as shown in Table 1, is quite dependent upon the number of peaks observed. As that number increases, the error in each peak influences the error in other peaks and the total error increases. Although it has proven difficult to sort out the errors caused by sampling problems from those due to instrumental problems, data of adequate reproducibility is readily available.

Another problem with this technique results from the fact that some samples do not efficiently couple with laser radiation. As mentioned previously, initial absorption is necessary for plasma generation; should this not occur (as is the case, at times, with white crystalline solids), laser pulsing results in no apparent product formation. This problem has been long recognized and has been addressed using two approaches. Either the sample has been placed upon a substrate that does absorb [2] or absorbing centers have been incorporated in the sample [7] prior to analysis. The first of these approaches complicates the pyrolysis process by spreading the pulse width of the thermal event. Adequate thermal conductivity must be maintained across the sample-substrate boundary as well. This technique will probably seldomly be used. Initially, several studies appeared describing the use of carbon as a material to provide absorbing centers. This approach markedly changes [21] the product distribution both in the low molecular weight gas ensemble and in the thermal blow off fragmentation products. More recently, it has been shown [22] that powdered nickel is a sensible way to incorporate absorbing centers. One simply thoroughly mixes nickel metal with the sample of interest and then pyrolyzes. The resulting pattern is not influenced by the addition of this type of absorbing center.

This technique removes the one severe limitation of laser-induced pyrolysis.

It has been argued that high temperature distributions can be successfully frozen out of laser-induced plasmas [10]. Our data shows that high temperature, equilibrium thermodynamic distributions are found upon analysis of the plasma-quenched ensemble of low molecular weight gases [16]. The implications of this fact are that, at least for simple systems, an analysis of the concentrations of these gases gives a rapid and straightforward characterization of the sample. We have termed this Plasma Stoichiometric Analysis (PSA) [22].

The basis of this technique is shown in Figure 3 for a binary molecular system-hydrocarbons. We consider again laser induced heating to produce an energetic plasma which is rapidly quenched, rapidly enough to freeze a high temperature distribution. The plasma quenched ensemble consists of a series of low molecular weight gases ranging in increasing hydrogen activity from carbon through several hydrocarbons to hydrogen. If we select a temperature near 3500 K for the "temperature" of the quenched distribution, we would find that the major products should be  $C(g)$ , hydrogen and acetylene. However this does not consider the stoichiometry of the plasma but assumes unit activities of each element in that system. Acetylene is a sensitive indicator of such plasma stoichiometry. Carbon-rich systems yields high fractions of this gas. As the hydrogen fraction increases, the acetylene fraction decreases. In Figure 4, results are shown for the hydrocarbon

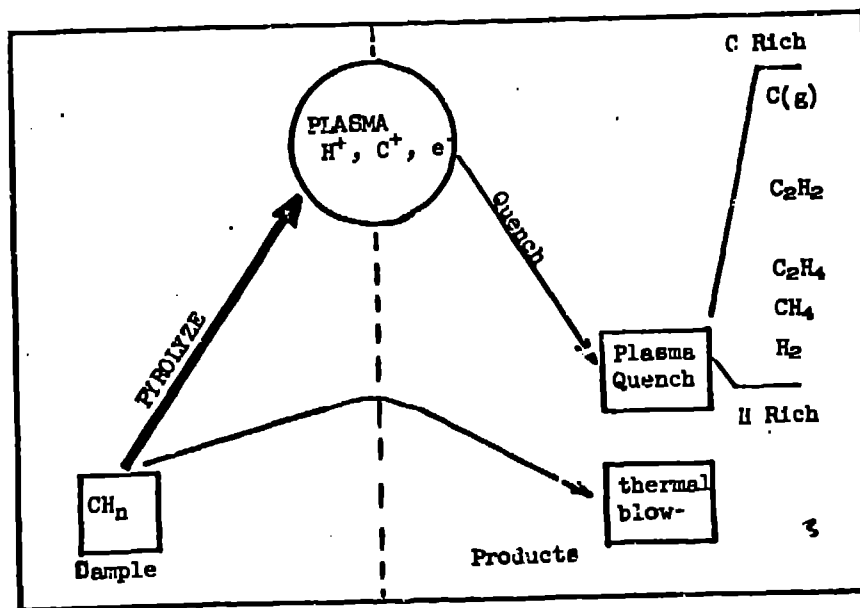


Fig. 3. Representation of Quenching Routes for Binary Hydrocarbons: Plasma Stoichiometric Analysis.

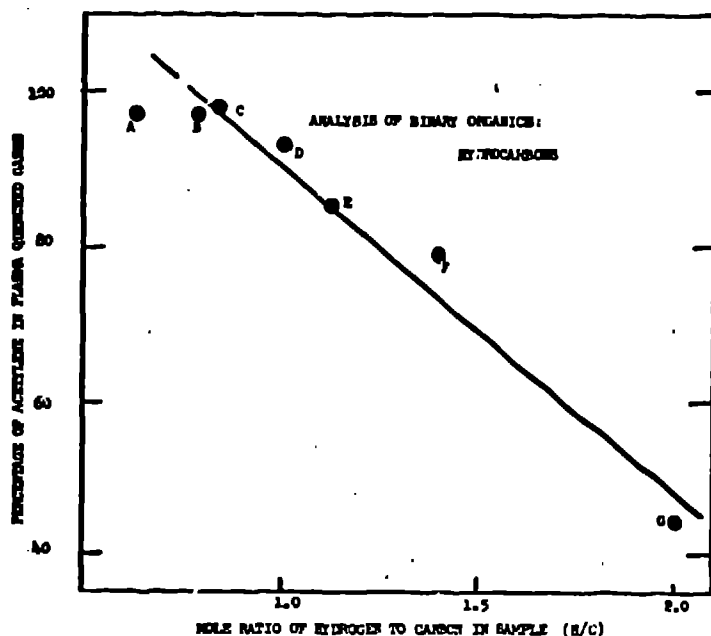


Fig. 4. Example of Plasma Stoichiometric Analysis - the Binary Case. Percentage of acetylene in the low molecular gas ensemble compared to the molar H/C ratio in sample.

- A = Phenanthrene
- B = Terphenyl
- C = Napthalene
- D = 1,2-diphenylethane
- E = Polystyrene
- F = Durene
- G = paraffin

system. The percentage of acetylene is shown plotted versus the hydrocarbon to carbon ratio in the sample. The results are well predicted by assuming a quenching "temperature" near 3500 K.

This temperature may be the maximum temperature of the plasma. Unlike other systems manufactured in high vacuum, generation of a laser induced plasma in helium gas (as done here) could lead to decreased plasma temperatures. The temperature may also be an indication of the energy of the system at the first instance that stable chemical bonds form. Following that time, the quenching process is rapid enough to preclude additional transformation. In any case, ample evidence suggests that the low molecular weight product distribution can be well predicted by equilibrium thermodynamics. And, conversely, using measured data of product distribution and referring to generated data from chemical thermodynamics, one can determine the nature of the sample.



## UTILITY OF LASER PYROLYSIS

Consider now some of the applications of this technique. Polymer characterization has been mentioned previously. Figure 5 shows results for a series of quinoxalines, high temperature-stability organic materials. These results were accomplished by ruby pyrolysis. In each case initially low molecular weight gases result from the plasma quenching process. Each of the quinoxalines then yields a highly characteristic fragmentation pattern.

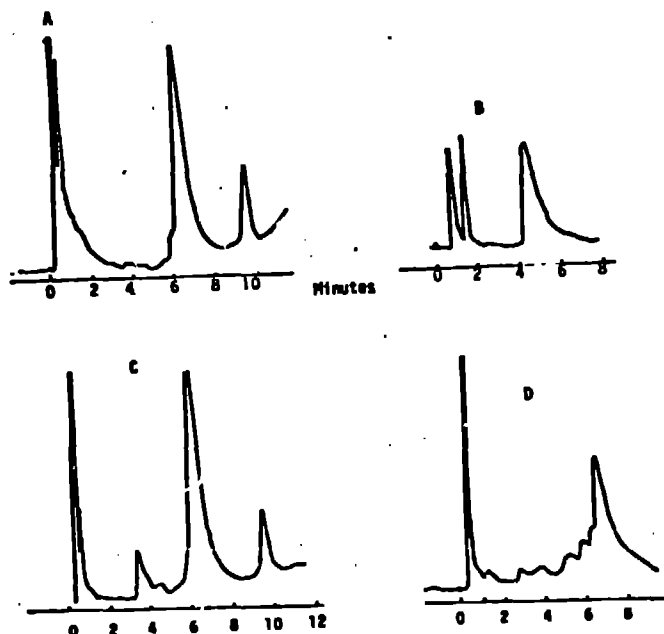


Fig. 5. Representative Laser Pyrograms Resulting from Ruby Deposition into Temperature Stable Quinoxaline Compounds. First peak is unresolved mixture of low molecular weight gases (plasma quenched ensemble) followed by thermal blow off products. Column: 10% Apiezon N on 60-80 ABS; 75-350°C, Carrier Flow 20 ml He/min.

- A. 5,6-dimethyl-2,3-di (2-pyridyl) quinoxaline.
- B. 1,4-di (2-quinoxalyl) benzene.
- C. poly(2,2-(1,4-phenylene)-6,6-bisquinoxaline)
- D. 2,3-dimethylquinoxaline.

Laser pyrolysis has also been shown well suited for the characterization of naturally occurring carbonaceous materials. Our studies concentrated on oil shales from the Green River Formation in the Western United States [23]. These shales are a Marlstone type of rock incorporating organic material ranging up to 15% by weight. The carbonaceous material is intimately associated with mineral matter; these organics show a vast predominance of aliphatic compounds upon retorting and a H/C ratio close to 1.6. Laser

pyrolysis on these materials results in a complex mixture of products. Consider only the low molecular weight gases as shown in Figure 6. Here results are shown for two simultaneous detectors. The FID, the lower trace, shows a response for methane, acetylene and ethylene. The upper trace shows that the major products hydrogen and carbon monoxide are not neglected by the FID. Efforts have concentrated on using these low molecular weight gases for the need in oil shale characterization center on rapid methods to replace the time consuming Fischer assays.

The first task is to develop a rapid method to assay the material. The carbon in these materials is of two types, organic carbon in the hydrocarbons and inorganic, incorporated as carbonates in the rock matrix. Free energy calculations suggest that as the hydrocarbon content increases, the fraction of ethylene found in the low molecular weight gases will increase

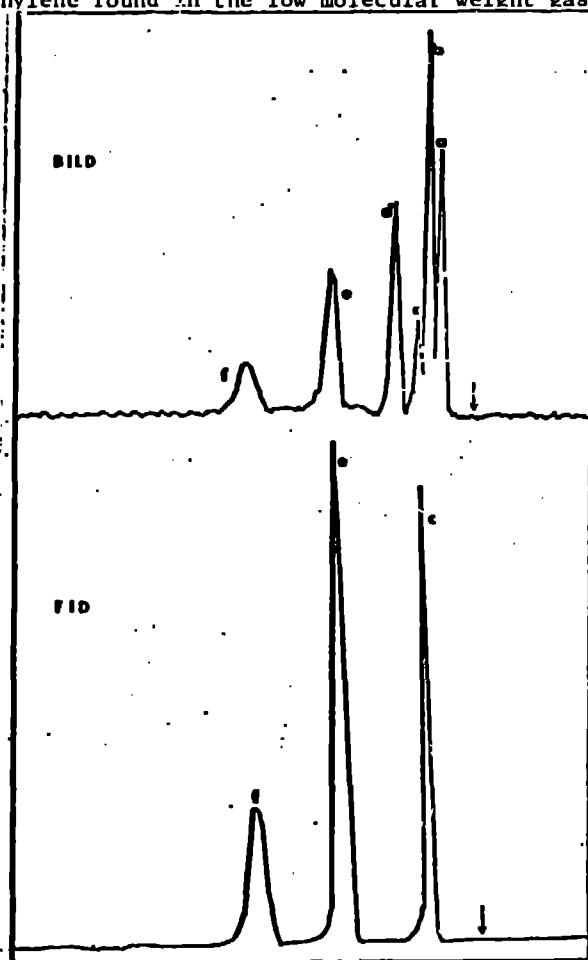


Fig. 6. Laser pyrograms from Green River oil shale sample. Separation of low molecular weight gases. Upper trace- BILD detector; lower trace-FID detector. Peak identification: a= $H_2$ , b=CO, c= $CH_4$ , d= $CO_2$ , e= $C_2H_2$ , f= $C_2H_4$ . Higher molecular weight fragments are not eluted in times shown here.

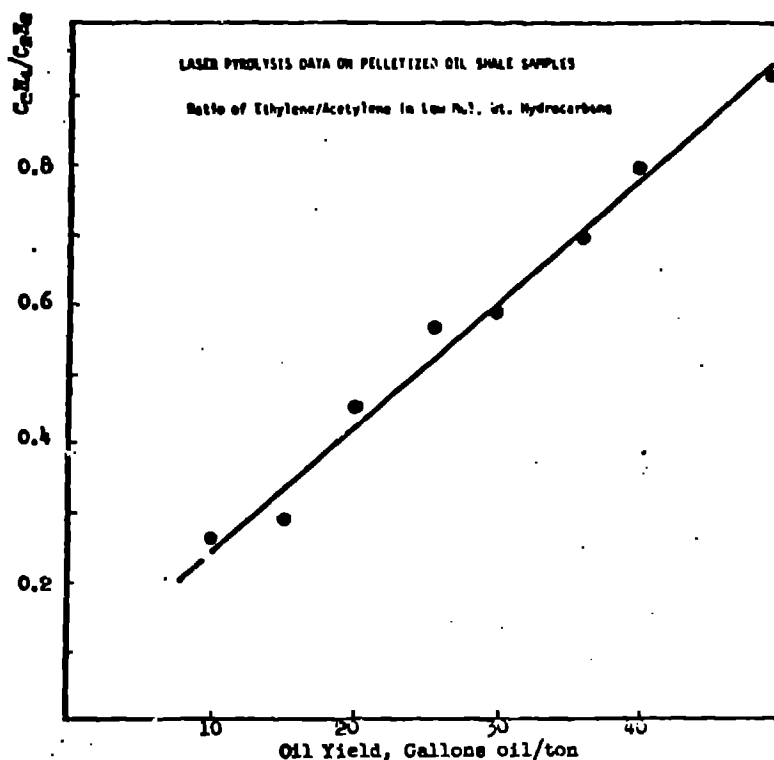


Fig. 7. Laser pyrolysis gas chromatography data for Green River oil shales. Comparison of the ratio of ethylene/acetylene in the low molecular weight gas pyrolysis products to the measured (Fischer assay) oil yields.

accordingly [24]. This is shown in Figure 7 which shows the ratio of ethylene/acetylene is a sensitive measure of oil content of the shale. By normalizing the data in this way, variations in pulse to pulse intensities are minimized. Water is also a pyrolysis product although analysis conditions used in Figure 6 precluded the elution of that compound. If one does compare the intensity of the water peak and compares that to known gravimetric values for that compound, data such as are shown in Figure 8 result. Likewise our studies have shown that these results predict H/C ratios in these materials and can be used to distinguish between organic and inorganic carbon. Certainly each of these tasks can be done by other methods; some can be done more accurately by other methods. However, lpgc offers a convenient, rapid method for characterization of samples of this type. Pyrolysis and quantification of these low molecular weight gas mixtures is a task that can be done in a few minutes, if not a few seconds. It has been recommended that only the total hydrocarbon content be measured using a hydrocarbon monitor utilizing no prior separation. Certainly, if one is simply after the oil yield, this technique will give in a few seconds

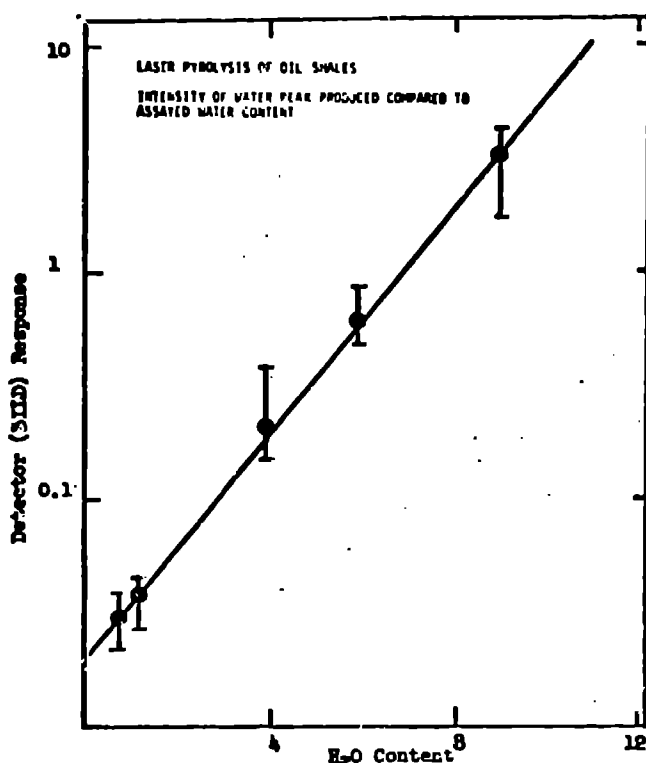


Figure 8. Laser pyrolysis-gas chromatography analysis of Green River Oil Shales: Analysis of water content. Comparison of detector (BILD) response for intensity of water peak compared to water content (gallons/ton) in standard samples.

results that compare favorably in precision with those determined with classical Fischer assay methods.

Studies have also been done on samples of coals. Table 2 shows the coals considered for these investigations. Two lignites were selected, two bituminous coals and one subbituminous sample. Table 3 lists analysis of the low molecular weight gases, methane, acetylene, hydrogen and carbon monoxide for these five coal samples and compares these data to calculated values determined assuming the atomic ratios taken from Table 2 and assuming a quenching temperature of 3300 K. These calculations assume that the gaseous carbon ( $C_{(g)}$ ) is quenched to a nonvolatile film in the pyrolysis chamber and that the ( $C_2H\cdot$ ) fragment combines with  $C_2H_2$  to form acetylene while  $H\cdot$  couples to form  $H_2$  and to increase the yield of molecular hydrogen.

The yields of methane are far higher than predicted. We assume that this simply reflects the methane incorporated in these coals, i.e., methane predominately is a thermal blow off product. Since methane content of these powdered materials is highly dependent upon sample history, these data probably are not suggestive of the methane incorporated in the

Table 2

Analysis of Coal Samples (Ultimate Analysis); Values Calculated on a Moisture-free Basis

Sample Number	1	2	3	4	5
Sample Type	Lignite (Texas)	Subbituminous (New Mexico)	Lignite (Louisiana)	Bituminous Ill. #6	Bituminous Central Illinois #6
% Carbon	43.11	65.26	60.10	72.21	65.40
% Hydrogen	3.39	4.73	4.23	5.03	4.59
% Nitrogen	0.73	1.07	1.26	1.29	1.08
% Chlorine	0.03	0.07	0.14	0.04	0.06
% Sulfur	2.45	1.47	0.83	2.99	4.41
% Oxygen	11.96	12.78	14.60	9.60	8.65
% Ash	38.26	14.62	18.04	8.84	15.61

Analysis data supplied by Paul Weir Company, Chicago, Illinois.

Table 3

Plasma Stoichiometric Analysis - Comparison of Measured Low Molecular Weight Gases to that Composition Predicted at 3300 K on Five Coal Samples (All values in volume %)

Sample	Methane		Acetylene ( $C_2H_2 + C_2H$ )		Hydrogen ( $H_2 + H$ )		Carbon monoxide (CO)	
	Meas.	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.	Calc.
1	2.05%	$1.36 \times 10^{-3}$	15.3	15.6	44.5	46.1	22.9	26.4
2	3.70	$1.42 \times 10^{-3}$	20.5	20.3	46.6	46.7	20.9	21.5
3	1.93	$1.30 \times 10^{-3}$	17.4	18.2	50.2	47.8	25.1	25.9
4	3.05	$1.46 \times 10^{-3}$	22.1	23.7	51.4	47.2	17.7	16.2
5	3.83	$1.45 \times 10^{-3}$	22.0	23.4	45.4	47.0	21.7	15.8

original samples. However, they do suggest that lpgc may be a rapid method to analyze fresh coals for methane content. However the other calculated values agree favorably with those found by experiment. Data for acetylene yields is shown in Figure 9 which shows the calculated quantity of acetylene compared to that found by experiment. The calculated quantity is a sensitive measure of the atomic composition of the original material. By reference to these data, one can again determine the composition of this material to learn the H/C ratio, the methane content, the oxygen content, etc. These data clearly point to the validity of plasma quenching calculations and to the possibilities of laser induced pyrolysis.

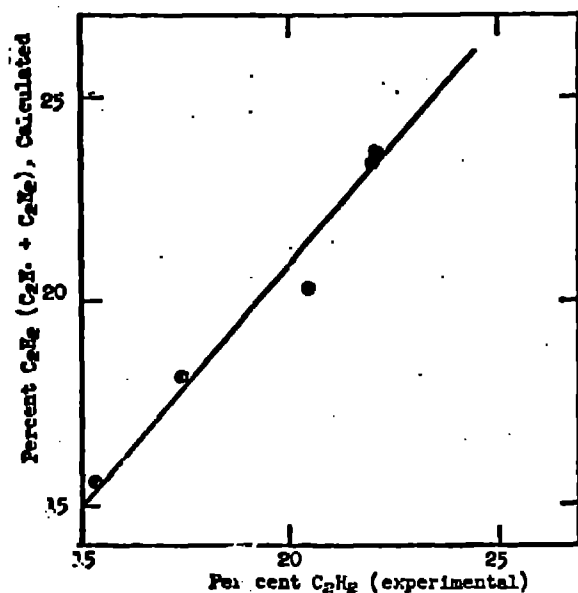


Fig. 9. Comparison of the percentage acetylene measured in the low molecular weight gases resulting from lpgc on five coal samples and that predicted from thermodynamic calculations assuming the plasma is quenched at 3300 K.

These discussions have concentrated upon the applications of the plasma quenched distribution. This has been done. Much of the other work covered here will stress the other use of laser induced pyrolysis- generation of characteristic molecular fragments.

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